Noble-gas–solid-surface beam-scattering spectroscopy in the eV range. Nuclear channel, formal theory

T. Maniv* and Morrel H. Cohen
The James Franck Institute, The University of Chicago, Chicago, Illinois 60637
(Received 13 July 1978)

We discuss the use of high-energy beams (i.e., in the eV range) of heavy noble-gas atoms to study surface dynamics for relatively high energy and momentum loss in both the nuclear and electronic channels. We give a general formulation of this problem for the nuclear channel, which can be generalized to include the electronic channel. The reflection probability is evaluated using the path-integral notation and applying semiclassical methods (stationary-phase approximation) on a multiple integral corresponding to a perturbationlike form of the reflection probability amplitude. The final form is locally similar to that predicted by the "rippling mirror" model (i.e., the dynamical Kirchhoff approximation), provided that the impulse approximation for the gas-surface dynamics holds. This similarity becomes global if the amplitude of the surface corrugation is much larger than the effective range of the gas-solid forces in the vicinity of the solid termination. The calculational procedure suggested by this formulation is tractable and is general enough to include anharmonic excitations such as desorption, structural damage, or low-energy sputtering as well as harmonic excitations (i.e., multiphonon excitations).

I. INTRODUCTION

The scattering of atomic beams from solid surfaces has developed rapidly as a method for investigating surface properties during the last few years. However, most of the effort in this field has been concerned with the low-energy regime far below the eV range, concentrating on elastic phenomena such as diffraction,[1] rainbow scattering,[2] and selective adsorption.[3,4] The information gained from these investigations is therefore limited to static or time-averaged properties of the surface.

Recently developed experimental techniques[4,5] provide well-defined monoenergetic beams of heavy atoms with energies in the eV range as well as detection systems that are capable of measuring the energy distribution of the scattered atoms[6] as well as their angular distribution. This progress opens the door to investigations of a variety of dynamical phenomena that can start on the surface during the collision, ranging from multiphonon excitations (in the harmonic limit) through desorption, structural damage or even low-energy sputtering (in the anharmonic limit) to electronic excitations on the surface. The domain of accessible momentum transfer is large and the extent of energy transfer is up to ~10 eV. The initial stages of the excitation process are confined strictly to the surface because of the short range of the gas-atom–surface interaction at these energies.

In the light of these considerations we discuss here the use of high-energy beams (i.e., in the eV range) of heavy noble-gas atoms (e.g., Ar) to study surface dynamics for relatively high energy and momentum loss in both the nuclear and electronic channels. This scheme has some significant advantages over the current methods for investigating the solid surface:

(i) Due to the relatively small polarizability of the noble-gas atom and the high energy involved, the penetration of the interaction into the solid is small compared to the range of the solid interatomic potential.

(ii) The beam is an inert probe of the surface excitations for relatively high energy because of the high threshold for exciting its internal degrees of freedom (e.g., 11.825 eV for Ar).

(iii) Energy in the eV range is much higher than the long-range attractive part of the atom-surface potential so that the beam is totally reflected from the short-range repulsive part of that potential without interference from any kind of adsorption on the surface.

There are only a few experimental investigations at this time that are relevant to our problem.[7,8,9] Typical angular distributions for the system Ar-Ag(111) are shown, for example, in Fig. 3 of Ref. 7. Each distribution is dominated by a single lobe near the specular direction while the lobe maximum is systematically shifted toward the surface tangent. Some measurements of energy distributions have been reported in Ref. 9.

The relevant theoretical calculations available at this time are limited either to model calculations such as the "hard cube" model[10] or to full-scale numerical calculations of the classical trajectories involved.[11] Oman's numerical calculations[11] exhibit a reasonable agreement with the current experimental results,[7] but the lack of flexibility as well as of physical insight associated with such extensive numerical calculations make

it inadequate for our purposes. The hard cube model is an extremely simple approximation, which provides much better physical insight than Oman's calculations. However, it suffers from a very serious limitation concerning its flat surface assumption. This assumption confines the surface atoms to move only in rigid, independent channels normal to the surface plane. Thus momentum transfer to vibrational modes parallel to the surface plane as well as to the solid as a whole via reciprocal-lattice vectors parallel to the surface plane is completely impossible in this model. This is a severe limitation for the high energies under consideration.

The purpose of this article is to propose a general theory for the above problem which could motivate further experimental and theoretical investigations. The final form of this theory should be sufficiently simple such that one can gain insight into the basic structure of the problem. Methods such as the standard semiclassical method[12,13] or the corrugated-hard-wall potential method,[14-16] which are currently used for the elastic channels with a considerable amount of success, seem to be, at least at first sight, less promising for the inelastic channels. The standard semiclassical method requires in its early stages extensive numerical calculations of classical trajectories and these become quite intractable when excitations of the enormous number of solid degrees of freedom become important. The various hard-wall methods, on the other hand, are much more tractable but their application to our problem should be carefully justified, especially because recoil effects of the surface atoms might be very important for the incident energies under consideration.

In this paper we show, however, that a hard-wall representation is a reasonable model in our case if the impulse approximation for the gas-surface dynamics during the collision event holds and if the effective range of the gas-surface forces is very small compared to the amplitude of the surface corrugation. This is shown by using a procedure which applies semiclassical methods to a time-dependent perturbationlike form for the reflection probability amplitude. The introduction of this form leads to a clear identification of a definite set of dynamical variables, characterizing the collision event. The application of the stationary phase method on this form converts these dynamical variables into well-defined parameters characterizing the collision and leads to a natural application of the impulse approximation. The result of this procedure is locally similar to the "rippling mirror" of Berry[17] and Garibaldi *et al.*[14] A global similarity is obtained when the effective range of the gas-surface forces is very small compared to the amplitude of the surface corrugation. We restrict ourselves in the present paper to inelastic processes associated with energy transfer to the nuclear channel, but the formulation we use here can be easily generalized to include the electronic channel. The latter will be done in a subsequent article. In Sec. II we consider the basic parameters characterizing our problem and discuss the approximations which can be made. In Sec. III we represent the general framework of our theory in terms of the path-integral notation. The prescription for solving the problem is illustrated in Sec. IV A by means of a relatively simple example of a static solid. The limitations of this prescription are discussed in Sec. IV B. In Sec. V we apply our prescription on the more general case of a moving solid and in Sec. VI we discuss the results, and summarize this paper.

II. GENERAL CONSIDERATIONS

The problem under consideration can be characterized by three intrinsic lengths:

(i) The wavelength λ of the incident beam

$$\lambda = 2\pi\hbar/(2M_G E_i)^{1/2},$$

where E_i is the incident energy of the gas atom and M_G its mass.

(ii) The effective range c of the gas-surface forces, namely, the size of the region in which the solid-gas interaction V varies considerably,

$$c \equiv \left| V/\nabla V \right|_{V=E_i}.$$

(iii) The interatomic distance a in the solid surface.

The length hierarchy in this problem is

$$\lambda \ll c \ll a$$

such that two significant approximations can be made:

(i) The semiclassical approximation for the nuclear motion during the collision.

(ii) The impulse approximation for the gas-solid dynamics during the collision.

The first approximation is readily associated with the first inequality $\lambda \ll c$. By the impulse approximation we mean that the collision time is so short that the interaction among the solid atoms can be regarded as constant during the collision, namely, that

$$(\Delta U/\Delta E_{\mathrm{kin}}) \ll 1,$$

where ΔU is the change in the solid potential energy and ΔE_{kin} is the corresponding change in the solid kinetic energy during the collision. This can be shown to be associated with the second inequality, $c \ll a$ (see Sec. III).

III. FORMULATION

We describe the combined gas-atom–solid system by the Lagrangian

$$\mathcal{L}\{\vec{\mathbf{r}}\dot{\vec{\mathbf{r}}},\{q\}\{\dot{q}\}\}=\mathcal{L}_A\{\dot{\vec{\mathbf{r}}}\}+\mathcal{L}_S\{\{q\}\{\dot{q}\}\}-V(\vec{\mathbf{r}},\{q\}),$$

where $\mathcal{L}_A\{\dot{\vec{\mathbf{r}}}\}$ is the gas-atom Lagrangian, $\mathcal{L}_S\{\{q\}\{\dot{q}\}\}$ is the solid Lagrangian, and $V(\vec{\mathbf{r}},\{q\})$ is the atom-solid interaction. $\mathcal{L}_A$ consists of a single term corresponding to the atom translational kinetic energy. $\mathcal{L}_S$ is, however, a many-body Lagrangian consisting of the solid nuclear coordinates as well as its electronic coordinates. The totality of the solid coordinates is described by the multidimensional vector $\{q\}$.

The probability amplitude for the combined system to go from the event $a\equiv(\vec{\mathbf{r}}_a,\{q\}_a,t_a)$ to the event $b\equiv(\vec{\mathbf{r}}_b,\{q\}_b,t_b)$ is the path integral[18]

$$G(b,a)=\int_a^b\mathfrak{D}\vec{\mathbf{r}}\int_a^b\mathfrak{D}\{q\}\times\exp\left(\frac{i}{\hbar}\int_{t_a}^{t_b}\mathcal{L}_A\{\dot{\vec{\mathbf{r}}}\}\,dt-\frac{i}{\hbar}\int_{t_a}^{t_b}V(\vec{\mathbf{r}},\{q\})\,dt+\frac{i}{\hbar}\int_{t_a}^{t_b}\mathcal{L}_S\{\{q\}\{\dot{q}\}\}\,dt\right).\tag{1}$$

Defining unperturbed propagators by

$$G_A^{(0)}(\beta,\alpha)=\int_\alpha^\beta\mathfrak{D}\vec{\mathbf{r}}\exp\left(\frac{i}{\hbar}\int_{t_\alpha}^{t_\beta}\mathcal{L}_A\{\dot{\vec{\mathbf{r}}}\}\,dt\right),\tag{2a}$$

$$G_S^{(0)}(\beta,\alpha)=\int_\alpha^\beta\mathfrak{D}\{q\}\exp\left(\frac{i}{\hbar}\int_{t_\alpha}^{t_\beta}\mathcal{L}_S\{\{q\}\{\dot{q}\}\}\,dt\right),\tag{2b}$$

we may write G as

$$G(b,a)=G^{(0)}(b,a)+\int_{t_a}^{t_b}dt_2\int_{t_a}^{t_2}dt_1\int d\vec{\mathbf{r}}_1\int d\vec{\mathbf{r}}_2\int d\{q\}_1\int d\{q\}_2\,G^{(0)}(b,2)\,T(2,1)G^{(0)}(1,a),\tag{3}$$

where

$$G^{(0)}(\beta,\alpha)=G_A^{(0)}(\beta,\alpha)G_S^{(0)}(\beta,\alpha)$$

and the T-matrix above is given by

$$T(2,1)=-\frac{i}{\hbar}V(\vec{\mathbf{r}}_1,\{q\}_1)\delta(t_2-t_1)\delta(\vec{\mathbf{r}}_2-\vec{\mathbf{r}}_1)\times\delta(\{q\}_2-\{q\}_1)+\left(\frac{i}{\hbar}\right)^2V(\vec{\mathbf{r}}_2,\{q\}_2)\times G(2,1)V(\vec{\mathbf{r}}_1,\{q\}_1).\tag{4}$$

The major difficulty in this problem is that V is a strong interaction so that a perturbational expansion in V is very slowly convergent, if at all. The advantage of writing G in a perturbationlike form such as Eq. (3), however, is that it separates explicitly the pre-collision and post-collision events (i.e., $a\to1$, $2\to b$) from the collision event (i.e., $1\to2$) so that concepts like "collision propagator" $G(2,1)$ or "collision-time variable" (t_2-t_1) can be identified. As we shall see later, in the semiclassical approximation the collision-time variable (t_2-t_1) becomes a well-defined parameter characterizing the time duration of the collision, and this leads to a natural application of the impulse approximation. Note, however, that both the semiclassical and the impulse approximations are invalid as far as the electronic motion is concerned. In the adiabatic approximation one is able to separate the nuclear coordinates from the electronic ones so that the above two approximations can be applied to the nuclear motion. We shall not consider electronic excitations in the present paper.

Considering only the nuclear motion in the solid the Lagrangian $\mathcal{L}_S$ is written as

$$\mathcal{L}_S\{\{q\}\{\dot{q}\}\}=\frac{M_S}{2}\sum_n(\dot{\vec{\mathbf{q}}}^n)^2-\frac{1}{2}\sum_{n,n'}U(\vec{\mathbf{q}}^n\vec{\mathbf{q}}^{n'}),\tag{5}$$

where M_S is the mass of a solid atom and n,n' run over the solid sites. Let us now check under what conditions we are allowed to use the impulse approximation. To do that we make a classical estimate of the change in the solid potential

$$U(\{qq\})\equiv\frac{1}{2}\sum_{n,n'}U(\vec{\mathbf{q}}^n\vec{\mathbf{q}}^{n'})$$

during the collision; the relevant part of this change is due to displacements of at most a few atoms on the surface which are directly impinged upon by the gas atom. Roughly speaking, the change in the solid potential during the collision can be written to first order as

$$\Delta U\sim\nabla U\Delta q,$$

where Δq is a typical displacement for a target atom, while the corresponding change in the kinetic energy is

$$\Delta E_{\text{kin}}\sim\tfrac{1}{2}M_S(\Delta q/\tau)^2,$$

where τ is the collision time. For a solid atom initially at rest the gain of momentum during the collision is

$$M_S\Delta q/\tau\sim\hbar k,$$

where k is the momentum loss of the gas atom. Thus together with the relation $\hbar k \sim \tau |\nabla V|$ we get that

$$\left| \frac{\Delta U}{\Delta E_{\rm kin}} \right| \sim \frac{|\nabla U| \tau}{\hbar k} \sim \frac{|\nabla U|}{|\nabla V|} \sim \frac{|U|}{|V|} \frac{c}{a},$$

where $|V| \sim E_i$. E_i in our problem is in the eV range so that for the usual case V is of the order of the solid cohesive energy, namely, $V \sim |U|$. Thus since $c \ll a$ we finally have

$$|\Delta U/\Delta E_{\rm kin}| \ll 1,$$

which ensures the validity of the impulse approximation.

The implication of this approximation is that the solid action integral can be written as

$$\int_{t_1}^{t_2} \mathfrak{L}_S\{\{q\}\{\dot{q}\}\}\, dt \approx \frac{M_S}{2} \sum_n \int_{t_1}^{t_2} (\dot{q}^n)^2\, dt - (t_2 - t_1) U(\{qq\}_1). \tag{6}$$

Substituting this expression into the path integral describing the collision propagator $G(2,1)$ we get

$$G(2,1) \approx e^{-(i/\hbar)(t_2 - t_1) U(\{qq\}_1)} g(2,1) \tag{7}$$

where

$$g(2,1) = \int_1^2 \mathfrak{D}\{q\} \int_1^2 \mathfrak{D}\vec{\mathbf{r}} \exp\left\{ \frac{i}{\hbar} \int_{t_1}^{t_2} \left[\frac{M_G}{2} (\dot{\vec{\mathbf{r}}})^2 + \frac{M_S}{2} \sum_n (\dot{\vec{\mathbf{q}}}^n)^2 - V(\vec{\mathbf{r}}, \{q\}) \right] dt \right\}.$$

We have reduced our problem to a scattering problem consisting of a single particle interacting with a target of many noninteracting particles.

The next step is to apply the semiclassical approximation.[19] $g(2,1)$ is written

$$g(2,1) = A(2,1) e^{(i/\hbar) S(2,1)}, \tag{8}$$

where $S(2,1)$ is a solution of the Hamilton-Jacobi equation

$$\frac{1}{2M_G} (\nabla_{\vec{\mathbf{r}}_2} S)^2 + \frac{1}{2M_S} \sum_n (\vec{\nabla}_{\vec{\mathbf{q}}_2^n} S)^2 + V(\vec{\mathbf{r}}_2, \{q\}_2) + \frac{\partial}{\partial t_2} S = 0 \tag{9a}$$

and $A(2,1)$ is the corresponding solution of the continuity equation

$$\mathrm{div}_{\vec{\mathbf{r}}_2} \left(\frac{A^2 \vec{\nabla}_{\vec{\mathbf{r}}_2} S}{M_G} \right) + \sum_n \mathrm{div}_{\vec{\mathbf{q}}_2^n} \left(\frac{A^2 \vec{\nabla}_{\vec{\mathbf{q}}^n} S}{M_S} \right) + \frac{\partial}{\partial t_2} A^2 = 0. \tag{9b}$$

IV. STATIC SOLID

A. Formal solution

To gain more insight into the structure of the Hamilton-Jacobi equation we consider here the relatively simple case of a static solid. For this case the momenta of the solid atoms ($\vec{\nabla}_{\vec{\mathbf{q}}^n} S$) vanish and $V(\vec{\mathbf{r}}, \{q\})$ is independent of $\{q\}$. The corresponding Hamilton-Jacobi equation is

$$\frac{1}{2M_G} (\vec{\nabla}_{\vec{\mathbf{r}}_2} S)^2 + V(\vec{\mathbf{r}}_2) + \frac{\partial}{\partial t_2} S = 0. \tag{10}$$

A solution of this equation is given by[19]

$$S_c(\vec{\mathbf{r}}_2, \vec{\mathbf{r}}_1, \tau) = \int_{t_1}^{t_2} \mathfrak{L}\{\vec{\mathbf{r}}_c(t), \dot{\vec{\mathbf{r}}}_c(t), t\}\, dt, \tag{11a}$$

where

$$\mathfrak{L}\{\vec{\mathbf{r}}, \dot{\vec{\mathbf{r}}}, t\} = \mathfrak{L}\{\vec{\mathbf{r}}, \dot{\vec{\mathbf{r}}}\} = \frac{M_G}{2} (\dot{\vec{\mathbf{r}}})^2 - V(\vec{\mathbf{r}}), \quad \tau = t_2 - t_1$$

and $\vec{\mathbf{r}}_c(t)$ is a classical trajectory between $\vec{\mathbf{r}}_2 = \vec{\mathbf{r}}_c(t_2)$ and $\vec{\mathbf{r}}_1 = \vec{\mathbf{r}}_c(t_1)$. The corresponding solution for the continuity equation is given by[20]

$$A_c^2 = -\det(\partial^2 S/\partial \vec{\mathbf{r}}_1 \partial \vec{\mathbf{r}}_2)/2\pi i \hbar. \tag{11b}$$

Thus the general solution for the propagator g is a sum

$$g \equiv A e^{(i/\hbar) S} = \sum_c A_c e^{(i/\hbar) S_c} \tag{12}$$

over the totality of the classical trajectories between $\vec{\mathbf{r}}_1$ and $\vec{\mathbf{r}}_2$. When τ approaches zero, S approaches the limiting form[18]

$$\lim_{\tau \to 0} S(\vec{\mathbf{r}}_2 \vec{\mathbf{r}}_1, \tau) = \frac{M_G}{2} \frac{(\vec{\mathbf{r}}_2 - \vec{\mathbf{r}}_1)^2}{\tau} - \tau V\left(\frac{\vec{\mathbf{r}}_2 + \vec{\mathbf{r}}_1}{2} \right) \tag{13}$$

and the first term in the sum in Eq. (12), corresponding to the so-called "direct trajectory,"[21] becomes more and more important and finally dominates the sum. In the limiting form of S given by Eq. (13) there is a clear distinction between the contribution of the kinetic energy and that of the potential energy. For a finite τ the identification of these two contributions in S become less clear. Formally we can regard the two terms in the right-hand side of Eq. (13) as the starting terms in a Laurent expansion of S in powers of τ; by assimilating higher order terms in τ into the "bare" potential V we can write

$$S(\vec{\mathbf{r}}_2 \vec{\mathbf{r}}_1, \tau) = \frac{M_G}{2} \frac{(\vec{\mathbf{r}}_2 - \vec{\mathbf{r}}_1)^2}{\tau} - \tau \overline{V}(\vec{\mathbf{r}}_2 \vec{\mathbf{r}}_1, \tau), \tag{14}$$

where the renormalized potential $\overline{V}(\vec{\mathbf{r}}_2 \vec{\mathbf{r}}_1, \tau)$ is a regular analytic function of τ obeying

$$\lim_{\tau \to 0} \overline{V}(\vec{\mathbf{r}}_2 \vec{\mathbf{r}}_1, \tau) = V(\vec{\mathbf{r}}) + O(\tau^2), \tag{14'}$$

where[22]

$$\vec{r} \equiv \tfrac{1}{2}(\vec{r}_2 + \vec{r}_1) .$$

By substituting Eq. (14) into the Hamilton-Jacobi equation one gets an equation for the renormalized potential $\overline{V}$, which can be solved by successive iterations in an analytic expansion in powers of τ and $\vec{\rho} \equiv \vec{r}_2 - \vec{r}_1$. This may be a useful prescription if $V(\vec{r})$ is a polynomial since the spatial part of the iterative process terminates in this case after a finite number of iterations. For example, if $V(\vec{r})$ is a linear function we get for $\overline{V}$

$$\overline{V}(\vec{r}_2\vec{r}_1, \tau) \equiv \overline{V}(\vec{r}\vec{\rho}, \tau) = V(\vec{r}) + \frac{\tau^2}{24M_G}[\vec{\nabla}_{\vec{r}} V(\vec{r})]^2 .$$

It should be noted, however, that the repulsive part of the surface potential is very different from a polynomial. Despite this disadvantage the form suggested by Eq. (14) is very useful from the formal point of view, as we shall see later.

Using the phase function S from Eq. (14) for the propagator g and substituting g into Eq. (3) we have, after Fourier transforming from the external coordinates $\vec{r}_a, \vec{r}_b$ to the momenta $\vec{p}_a = \vec{p}$, $\vec{p}_b = \vec{p}'$,

$$\begin{aligned}\Delta G(\vec{p}', t_b; \vec{p}, t_a) &\equiv G(\vec{p}', t_b; \vec{p}, t_a) - G^{(0)}(\vec{p}, t_b - t_a) - G^{(1)}(\vec{p}', t_b; \vec{p}, t_a) \\ &= -\frac{1}{\hbar^2}\int_{t_a}^{t_b} dt_2 \int_{t_a}^{t_2} dt_1 G^{(0)}(\vec{p}', t_b - t_2) G^{(0)}(\vec{p}, t_1 - t_a) \\ &\quad \times \int d\vec{r}\, e^{i\vec{k}\cdot\vec{r}} \int d\vec{\rho}\, e^{-i\vec{p}\cdot\vec{\rho}} A(\vec{r}\vec{\rho}, \tau) V(\vec{r} + \tfrac{1}{2}\vec{\rho}) V(\vec{r} - \tfrac{1}{2}\vec{\rho}) \\ &\quad \times \exp\left(\frac{iM_G}{2\hbar}\frac{\rho^2}{\tau} - \frac{i}{\hbar}\tau\overline{V}(\vec{r}\vec{\rho}, \tau)\right), \end{aligned} \tag{15}$$

where $G^{(1)}$ is the first order term in the perturbation expansion[23] (Eq. 4), $\vec{k} \equiv \vec{p} - \vec{p}'$ and $\vec{\bar{p}} \equiv \tfrac{1}{2}(\vec{p} + \vec{p}')$.

At this stage we introduce the crucial approximations of this section, namely, the stationary phase approximation for the integrations over the space-time collision variables $\vec{\rho}, \vec{r}$ and $\tau = t_2 - t_1$. The validity of this approximation can be justified by the following consistency argument: The collision-time parameter τ_0, which will be determined by the stationary phase method later in this section, is of the order $\hbar k/|\nabla V|$ whence the exponent $\frac{1}{2}M_G\rho^2/\tau \sim M_G\rho^2|\nabla V|/2\hbar k$. The amplitude of the integrand in Eq. (15) includes the factor $V(\vec{r} + \frac{1}{2}\vec{\rho})V(\vec{r} - \frac{1}{2}\vec{\rho})$, which varies considerably where $\vec{r}$ is in the close vicinity of the surface and $\rho \lesssim c$. Thus the range of the variation of $\frac{1}{2}M_G\rho^2/\tau$ is of the order kc, which is very large compared to unity, provided that the situation of grazing incidence and emergence is excluded. This determines the scale of the total exponent in Eq. (15) to be very large compared to one and so justifies the validity of the stationary phase approximation. There are, however, some special situations for which this approximation fails, and we shall discuss them in Sec. IV B.

We first perform the integration over ρ. The value of ρ which makes the phase stationary is given by

$$\vec{\rho}_0 = \tau\frac{\hbar\vec{\bar{p}}}{M_G} + \tau^2\left(\frac{\partial}{\partial\vec{\rho}}\overline{V}\right)_{\vec{\rho}=\vec{\rho}_0} \Big/ M_G \tag{16}$$

and the value of the phase at $\vec{\rho} = \vec{\rho}_0$ is given by

$$\frac{1}{\hbar}S(\vec{r}\vec{\rho}_0, \tau) - \vec{p}\cdot\vec{\rho}_0 = \frac{1}{\hbar}\left[\tau^3\left(\frac{\partial}{\partial\vec{\rho}}\overline{V}\right)^2_{\vec{\rho}=\vec{\rho}_0} \Big/ M_G - \tau\overline{V} - \tau\hbar^2\bar{p}^2/2M_G\right]. \tag{16'}$$

$$\Delta G(\vec{p}', t_b; \vec{p}, t_a) \approx \Delta(\epsilon_p \epsilon_{p'}) \int d\tau \int d\vec{r}\, e^{i\vec{k}\cdot\vec{r}}\, B(\vec{r}, \tau) \exp\left(\frac{i}{\hbar}(\epsilon_p - \epsilon_{\bar{p}} - \overline{V})\tau + \frac{i}{\hbar}\tau^3\overline{V}^2_{\vec{\rho}}/2M_G\right), \tag{17}$$

where

$$\Delta(\epsilon_p \epsilon_{p'}) = \exp\left(\frac{i}{\hbar}\epsilon_p T\right)\left[\frac{e^{(i/\hbar)(\epsilon_{p'} - \epsilon_p)T} - 1}{\epsilon_{p'} - \epsilon_p}\right];$$

$$\tau \equiv t_b - t_a \tag{17a}$$

$$B(\vec{r}, \tau) = -\frac{1}{\hbar^2}\left(\frac{-2\pi i\hbar\tau}{M_G}\right)^{3/2} \times \left\{\det\left[\vec{I} - \frac{\tau^2}{M_G}\left(\frac{\partial^2\overline{V}}{\partial\vec{\rho}\partial\vec{\rho}}\right)_{\vec{\rho}=\vec{\rho}_0}\right]\right\}^{-1/2} A(\vec{r}\vec{\rho}_0, \tau), \tag{17b}$$

and $\epsilon_{\vec{p}} = \hbar^2 p^2 / 2M_G$.

The next integration is performed over $\bar{z}$—the component of $\vec{\mathbf{r}}$ normal to the "surface plane"; we again use the stationary phase method and the result is

$$\Delta G(\vec{p}', \vec{p}, T) \approx \Delta(\epsilon_{\vec{p}} \epsilon_{\vec{p}'}) \int d^2 \vec{R} e^{i\vec{K}\cdot\vec{R}} \int d\tau\, C(\vec{R}, \tau) \exp\left(\frac{i}{\hbar} (\epsilon_{\vec{p}} - \epsilon_{\vec{p}'}) \tau + i k_z \zeta(\vec{R}, \tau) \right), \tag{18a}$$

where $\vec{R}$ is the projection of $\vec{\mathbf{r}}$ on the surface plane, $\vec{K}$ is the projection of $\vec{k}$ on this plane,

$$\zeta(\vec{R}, \tau) = \bar{z}_0(\vec{R}, \tau) - \left(W \Big/ \frac{\partial}{\partial \bar{z}} W \right)_{\bar{z}=\bar{z}_0}, \tag{18b}$$

$$W(\vec{r}, \tau) = \bar{V}(\vec{r}\vec{\rho}_0, \tau) - \frac{\tau^2}{2M_G} \left(\frac{\partial \bar{V}}{\partial \vec{\rho}} \right)^2, \tag{18c}$$

$$C(\vec{R}, \tau) = B(\bar{z}_0 \vec{R}, \tau) \left(-2\pi i \frac{\partial W}{\partial \bar{z}} \Big/ \hbar k_z \frac{\partial^2 W}{\partial \bar{z}^2} \right)^{1/2}, \tag{18d}$$

and $\bar{z}_0(\vec{R}, \tau)$ is the solution of the equation

$$\hbar k_z = \tau \frac{\partial}{\partial \bar{z}} W(\bar{z}\vec{R}, \tau). \tag{18e}$$

Equation (18e) expresses the conservation of momentum normal to the surface plane during the collision in terms of the renormalized potential W. Equation (18c) shows that this potential has limiting behavior similar to that expressed in Eq. (14′) for $\bar{V}$. Finally we integrate over time τ with the result:

$$\Delta G(\vec{p}', \vec{p}, T) \approx \Delta(\epsilon_{\vec{p}} \epsilon_{\vec{p}'}) \int d^2 \vec{R}\, D(\vec{R}) \times \exp[i k_z \zeta(\vec{R}) + i \vec{K} \cdot \vec{R}], \tag{19a}$$

where

$$\zeta(\vec{R}) = \bar{z}_0(\vec{R}, \tau_0) + [(\epsilon_{\vec{p}} - \epsilon_{\vec{p}'}) - W(\vec{R}, \tau_0)] / \frac{\partial}{\partial z} W(\vec{R}, \tau_0), \tag{19b}$$

$$D(\vec{R}) = C(\vec{R}, \tau_0) \left(2\pi i / \hbar k_z \frac{d^2}{d\tau^2} \zeta(\vec{R}, \tau = \tau_0) \right)^{1/2}, \tag{19c}$$

and τ_0 is the solution of

$$\epsilon_{\vec{p}} - \epsilon_{\vec{p}'} = \frac{\partial}{\partial \tau} [\tau W(\bar{z}_0, \tau)]. \tag{19d}$$

Equation (19d) expresses the conservation of energy during the collision in terms of the renormalized potential W.

Except for very special situations (i.e., grazing incidence and emergence), the momentum transfer normal to the surface plane k_z is of the order of the incident momentum p. This means that the exponential in Eq. (19a) is a rapidly oscillating function of $\vec{R}$ while the amplitude $D(\vec{R})$ varies smoothly. Thus Eq. (19a) is similar to the reflection coefficient obtained from a smoothly corrugated hard-wall surface potential.[14] The corresponding "effective mirror," specified by the "shape function" $\zeta(\vec{R})$, is, however, a local concept and depends on a specific classical trajectory such that both $\zeta(\vec{R})$ and the trajectory are determined self consistently from the set of equations (18e), (19b), and (19d).

Thus both $\zeta(\vec{R})$ and $D(\vec{R})$ depend on $\epsilon_{\vec{p}}$, $\epsilon_{\vec{p}'}$, and k_z so that in addition to the explicit dependence of ΔG on k_z, appearing in Eq. (19a), there is an implicit dependence on the above parameters through $\zeta(\vec{R})$ and $D(\vec{R})$. It can be shown, however, that if the surface under consideration is not too flat the implicit dependence through $\zeta(\vec{R})$ is much weaker than the explicit one. The reason for that is the following: The relevant part of the bare potential V is very steep, namely $c = |V/\nabla V|_{V=E_i} \ll a$ (see Sec. II). This property should also characterize the renormalized potential W as a function of $\vec{r}$. On the other hand, as a function of τ, W is a relatively smooth function, provided that we are not dealing with a classical trajectory which passes through a caustic (see Sec. IV B). Thus the solution $\bar{z}_0(\vec{R}, \tau, k_z)$ of Eq. (18e) is a very weak function of k_z and τ. Furthermore, the second term in the right-hand side of Eq. (19b) is, according to the above argument, of the order c. However, if the surface under consideration is not too flat the variation $2h$ of $\zeta(\vec{R})$ as a function of $\vec{R}$ is some fraction of a, which is much larger than c in our problem. Thus, to a first approximation, $\zeta(\vec{R})$ is independent of the initial and final momenta and the explicit dependence of ΔG on these parameters is much stronger than the implicit one through $\zeta(\vec{R})$.

B. Limitations

Two basic assumptions are inherent to the formulation given in Sec. IV A: The first is that the renormalized potential $\bar{V}(\vec{r}\vec{\rho}, \tau)$ is a regular analytic function of τ and the second assumption, which will be seen to be related to the first one, is that

the stationary phase method is a good approximation for the integrations over the dynamical variables characterizing the collision event.

We consider here a very simple example of a troublesome situation in which both of these assumptions do not hold: A reflection from a one-dimensional potential given by

$$V(z)=\tfrac{1}{2}M_G\omega^2 z^2\Theta(z)\,,$$

where $\Theta(z)$ is the standard step function. Consider two arbitrary points z_1, z_2 within the scattering region (i.e., $z_1, z_2>0$): There is no classical trajectory between these points which is not fully confined to the scattering region. If $t_2-t_1\equiv\tau<\pi/\omega$, such a trajectory always exists. For the initial condition, $z=0$ at $t=0$, the solution of the classical equation of motion in the scattering region is given by $z=z_0\sin\omega t$ and the corresponding classical action between z_1 and z_2 is

$$S(z_2z_1,t_2t_1)=\frac{M_G}{2}\int_{t_1}^{t_2}(\dot z^2-\omega^2z^2)\,dt$$

$$=\tfrac{1}{4}M_G\omega z_0^2[\sin(2\omega t_2)-\sin(2\omega t_1)]\,,$$

which after some algebra can be converted into[18]

$$S(z_2z_2,\tau)=\frac{M_G\omega}{2\sin(\omega\tau)}[(z_1^2+z_2^2)\cos(\omega\tau)-2z_1z_2]\,.$$

Thus the collision propagator for z_1, $z_2>0$ and $\omega\tau<\pi$ is given by

$$g(\bar z\zeta,\tau)=A(\tau)e^{(i/\hbar)S(\bar z\zeta,\tau)}\,, \tag{20a}$$

where

$$S(\bar z\zeta,\tau)=\frac{M_G\omega}{4}\zeta^2\cot(\omega\tau/2)-M_G\omega\bar z^2\tan(\omega\tau/2)\,, \tag{20b}$$

$$\bar z\equiv(z_1+z_2)/2\,,\quad \zeta\equiv z_2-z_1\,,$$

and

$$A(\tau)=\left(\frac{M_G\omega}{2\pi i\hbar\sin(\omega\tau)}\right)^{1/2}. \tag{20c}$$

If $\omega\tau>\pi$ there is no classical trajectory connecting z_2, z_1 if both of them are in the scattering region. Thus the semiclassical approximation for $g(\bar z\zeta,\tau)$ in the scattering region $\bar z>0$, $-\bar z<\zeta<\bar z$ is given by

$$g(\bar z\zeta,\tau)=\Theta(\pi-\omega\tau)A(\tau)e^{(i/\hbar)S(\bar z\zeta,\tau)}\,. \tag{21}$$

For $\omega\tau\ll1$ Eq. (20b) approaches the limiting form $\frac{1}{2}M_G\zeta^2/\tau-\frac{1}{2}\tau M_G\omega^2\bar z^2$ in agreement with (13), while the amplitude $A(\tau)$ diverges like $\tau^{-1/2}$. This singularity and the divergence of the kinetic energy part of S reflect the dominant role of the "direct trajectory" for a vanishingly small propagation time τ.[24]

Another kind of singularity appears when $\omega\tau=\pi$. In this case the singular term is the renormalized potential $\bar V$. This singularity reflects the dominant role of an "indirect trajectory," namely, a trajectory which passes through the classical turning point.

We now apply the procedure of Sec. IV A to calculate the reflection probability for the particular example mentioned above: The integration over ζ [similar to ρ in Eq. (15)] can be calculated exactly and the result is

$$\Delta G(-p,p)\propto\int d\tau[\cos(\omega\tau/2)]^{-1}\int d\bar z[V(\bar z)]^2\exp\left(\frac{i}{\hbar}\epsilon_p\tau-\frac{iM_G\omega}{\hbar}\tan(\omega\tau/2)\bar z^2+ik\bar z\right). \tag{22a}$$

The integration over $\bar z$ can also be performed exactly with the result

$$\Delta G(-p,p)\propto\int d\tau[\sin(\omega\tau)]^{-1/2}\cot^4(\omega\tau/2)$$

$$\times\exp\left\{i\frac{2\epsilon_p}{\hbar\omega}\cos(\omega\tau/2)+\frac{i}{\hbar}\epsilon_p\tau\right\}, \tag{22b}$$

which is also the result given by the stationary phase method. The integration over τ is not as simple as the former integrations. An application of the stationary phase method to this integral is troublesome; the phase is stationary at $\tau_0=\pi/\omega$ so that the reflection probability is zero while a total reflection is expected. This result agrees, however, with the well-known fault of the simple WKB approximation to predict any reflection in a one-dimensional system.[21,25] The trouble is due to the divergence of the renormalized potential $\bar V$ at $\tau=\tau_0$, which pushes the stationary point $\bar z_0=(\hbar p/M_G\omega)\cot(\omega\tau/2)$ out of the scattering region. This is always the case in a one-dimensional potential problem since the classical trajectory associated with the reflected wave always touches a classical turning point if the potential is one-dimensional. Thus our procedure breaks down for a completely flat surface. In the general case, however, where the surface is corrugated, there are only restricted domains on the surface plane for which the important scattering region is effectively one-dimensional, namely where the self-consistent surface specified by $\zeta(\vec{\bar R})$ is locally flat. The location of such a troublesome area is determined by the equation

$$\det\left(\frac{\partial^2\zeta}{\partial\vec{\bar R}\partial\vec{\bar R}}\right)=0\,, \tag{23a}$$

which in the Kirchhoff method is known as the equation determining the location of a caustic.[17] In the close vicinity of such a caustic the stationary phase approximation for the integral over $\vec{\vec{R}}$ in Eq. (19) breaks down, a result which is consistent with the breakdown of this approximation for the integrations leading to Eq. (19). The size ΔR of such a troublesome area can be estimated from the condition for the breakdown of the stationary phase approximation, i.e.,

$$k_z\left|(\Delta\vec{\vec{R}})\left(\frac{\partial^2\zeta}{\partial\vec{\vec{R}}\partial\vec{\vec{R}}}\right)(\Delta\vec{\vec{R}})\right|\lesssim 1\,. \tag{23b}$$

For a one-dimensional sinusoidal surface $\zeta(x) = h\sin(2\pi x/\alpha)$ condition (23b) means that

$$\Delta x\lesssim\frac{a}{2\pi}\left(\frac{\lambda}{h}\right)^{1/3} \tag{23c}$$

showing that the troublesome areas reduce to tiny islands if the amplitude h of the surface corrugation is sufficiently large on the scale of λ.

Since a caustic is responsible for rainbow scattering[17] we may conclude that our scheme is, in principle, capable of determining the approximate location of the corresponding rainbow pattern but is incapable of determining its intensity. It should be noted, however, that this limitation weakens when the solid dynamics becomes important, a situation which is our main interest in this paper.

We finally mention another limitation of our procedure, namely, that it is restricted to dealing with classical trajectories which hit the surface only once.[16] In these situations there is only a single solution $(\bar{z}_0, \tau_0)$ of Eqs. (18e), (19d) for given initial and final momenta. If the surface is sufficiently corrugated[13] and the angle of incidence is sufficiently large[13,16] an alternative classical trajectory which hits the surface several times could have the same initial and final momenta. This situation corresponds to an appearance of an alternative solution of Eqs. (18e), (19d) for the same initial and final momenta, but with a much longer collision time τ_0. The analysis of such a multiple-hit situation is beyond the scope of this paper.

V. INELASTIC SCATTERING

Returning to the more general situation where the solid atoms can move, we write a solution of Eq. (9a) in the form

$$S(2,1)=\frac{M_G}{2}\frac{\rho^2}{\tau}+\sum_n\frac{M_S}{2}\frac{(\vec{q}_2^{\,n}-\vec{q}_1^{\,n})^2}{\tau} - \tau\bar{V}(\vec{\vec{r}}\,\vec{\vec{p}},\{q\}_2\{q\}_1,\tau)\,. \tag{24}$$

We recall that $\bar{V}(\vec{\vec{r}}\,\vec{\vec{p}},\{q\}_2\{q\}_1,\tau)$ is the renormalized interaction potential related to the original potential $V(\vec{\vec{r}},\{q\})$ by equations similar to (11a), (12), (14) and by the limiting equation

$$\lim_{\tau\to 0}\bar{V}(\vec{\vec{r}}\,\vec{\vec{p}},\{q\}_2\{q\}_1,\tau)=V(\vec{\vec{r}},\{q\})+O(\tau^2)\,.$$

Thus in a manner similar to that of Sec. III we write

$$\begin{aligned}\Delta G(b,a)=\int_{t_a}^{t_b}dt_2\int_{t_a}^{t_2}dt_1\int d\vec{\vec{r}}\int d\vec{\vec{p}}\int d\{q\}_1\int d\{q\}_2\,G_A^{(0)}(\vec{\vec{r}}_b,t_b;\vec{\vec{r}}+\vec{\vec{p}}/2,t_2)\\ \times G_S^{(0)}(\{q\}_b,t_b;\{q\}_2,t_2)\,\bar{A}(\vec{\vec{r}}\,\vec{\vec{p}},\{q\}_2\{q\}_1,\tau)\\ \times\exp\left(\frac{i}{\hbar}S(2,1)-\frac{i}{\hbar}\tau U(\{q\}_1)\right)G_S^{(0)}(\{q\}_1,t_1;\{q\}_a,t_a)G_A^{(0)}(\vec{\vec{r}}_1,t_1;\vec{\vec{r}}_a,t_a)\,,\end{aligned} \tag{25}$$

where

$$\bar{A}(\vec{\vec{r}}\,\vec{\vec{p}},\{q\}_2\{q\}_1,\tau)\equiv-\frac{1}{\hbar^2}\,V(\vec{\vec{r}}+\vec{\vec{p}}/2,\{q\}_2)\,V(\vec{\vec{r}}-\vec{\vec{p}}/2,\{q\}_1)A(\vec{\vec{r}}\,\vec{\vec{p}},\{q\}_2\{q\}_1,\tau)\,.$$

Transforming the external coordinates to momentum space and performing the integral over $\vec{\vec{p}}$ we get

$$\begin{aligned}\Delta G(\vec{\vec{p}}\,',\{q\}_b,t_b;\vec{\vec{p}},\{q\}_a,t_a)\approx\int_{t_a}^{t_b}dt_2\int_{t_a}^{t_2}dt_1\int d\vec{\vec{r}}\int d\{q\}_1\int d\{q\}_2 e^{i\vec{\vec{k}}\cdot\vec{\vec{r}}}\\ \times\exp\left(\frac{i}{\hbar}\epsilon_p t_a-\frac{i}{\hbar}\epsilon_{p'}t_b-\frac{i}{\hbar}(\epsilon_p-\epsilon_{p'})t_2\right)G_S^{(0)}(\{q\}_b,t_b;\{q\}_2,t_2)\\ \times B(\vec{\vec{r}},\{q\}_2\{q\}_1,\tau)G_S^{(0)}(\{q\}_1,t_1;\{q\}_a,t_a)\\ \times\exp\left(\frac{i}{\hbar}\tau[\epsilon_p-\epsilon_{\bar{p}}-W(\vec{\vec{r}},\{q\}_2\{q\}_1,\tau)]\right.\\ \left.+\frac{iM_S}{2\hbar}\sum_n\frac{(\vec{q}_2^{\,n}-\vec{q}_1^{\,n})^2}{\tau}-\frac{i}{\hbar}\tau U(\{q\}_1)\right),\end{aligned} \tag{26}$$

where B and W are defined in a similar manner to the quantities defined by Eqs. (17b) and (18c) respectively. The solid propagator $G_S^{(0)}$ can be written[18]

$$G_S^{(0)}(\{q\}_2,t_2;\{q\}_1,t_1)=\sum_m e^{-(i/\hbar)\epsilon_m(t_2-t_1)}\phi_m(\{q\}_2)\times\phi_m^*(\{q\}_1)\Theta(t_2-t_1)\,, \tag{27}$$

where $\phi_m(\{q\})$ is an eigenfunction of the solid Hamiltonian corresponding to the energy eigenvalue ϵ_m and $\Theta(t_2-t_1)$ is the standard step function. Using the spectral representation (27) in Eq. (26) we get

$$\Delta G(\vec{p}',\{q\}b,tb;\vec{p},\{q\}a,ta)=\sum_{m,m'}\Delta(\epsilon_{pm},\epsilon_{p'm'})\phi_m^*(\{q\}_a)\phi_{m'}(\{q\}_b)\times\int d\vec{r}\,e^{i\vec{k}\cdot\vec{r}}\int d\tau\int d\{q\}_1\int d\{q\}_2\phi_m(\{q\}_1)\phi_{m'}^*(\{q\}_2)\times B(\vec{r},\{q\}_2\{q\}_1,\tau)\exp\left(i\sum_n\frac{M_S}{2\hbar\tau}(\vec{q}_2^{\,n}-\vec{q}^{\,n}{}_1)^2-\frac{i\tau}{\hbar}W(\vec{r},\{q\}_2\{q\}_1,\tau)\right)\times\exp\left(\frac{i}{\hbar}\tau[\epsilon_p-\epsilon_{\vec{p}}+\epsilon_m-U(\{q\}_1)]\right), \tag{28}$$

where $\epsilon_{pm}\equiv\epsilon_p+\epsilon_m$.

Let us consider now the multiple integral over $\{q\}_2$, namely,

$$\int d\vec{q}_2^{\,1}\cdots\int d\vec{q}_2^{\,N}B(\vec{r},\{q\}_2\{q\}_1,\tau)\phi_{m'}(\{q\}_2)\times\exp\left(i\sum_n\frac{M_S}{2\hbar\tau}\times(\vec{q}_2^{\,n}-\vec{q}_1^{\,n})^2-\frac{i\tau}{\hbar}W(\vec{r},\{q\}_2\{q\}_1,\tau)\right). \tag{29}$$

Within the important scattering region there is one or a few atomic sites which dominate the value of the "dressed" potential $W(\vec{r},\{q\}_2\{q\}_1,\tau)$; we denote such a site by the discrete function $n(\vec{r})$. It is clear that

$$\frac{\tau}{\hbar}\left|\frac{\partial}{\partial\vec{q}_2^{\,n}}W(\vec{r},\{q\}_2\{q\}_1,\tau)\right|\begin{matrix}\ll p;\quad n\neq n(\vec{r})\\ \sim p;\quad n=n(\vec{r})\,.\end{matrix} \tag{30}$$

Thus consider the integral

$$\int d\vec{q}_2{}^n B(\vec{r},\{q\}_2\{q\}_1,\tau)\phi_{m'}(\{q\}_2)\times\exp\left(\frac{iM_S}{2\hbar\tau}(\vec{q}_2^{\,n}-\vec{q}_1^{\,n})^2-\frac{i\tau}{\hbar}W\right). \tag{31}$$

The eigenfunction $\phi_{m'}(\{q\}_2)$ can be written

$$\phi_{m'}(\{q\}_2)=\exp\left[-\frac{i}{\hbar}\sum_n(\vec{q}_2^{\,n}-\vec{q}_1^{\,n})\cdot\hat{\vec{P}}_1^{\,n}\right]\phi_{m'}(\{q\}_1)\,, \tag{32}$$

where $\hat{\vec{P}}_1^{\,n}$ is the momentum operator $(\hbar/i)(\partial/\partial\vec{q}_1^{\,n})$ for the site n. As suggested by (30) the momentum transfer to an atom $n=n(\vec{r})$ is of the order p such that within the scattering region we expect a semiclassical behavior from the relevant atom. Thus we can treat $\hat{\vec{P}}_1^{\,n}$ as a classical quantity, namely we neglect any commutation associated with it. For $n\neq n(\vec{r})$ the momentum transfer during the collision is very small compared to p, and so the error introduced by neglecting nonvanishing commutators in the exponential is small. Thus our integral is

$$\int d\vec{q}_2^{\,n}B(\vec{r},\{q\}_2\{q\}_1,\tau)\times\exp\left(\frac{iM_S}{2\hbar\tau}(\vec{q}_2^{\,n}-\vec{q}_1^{\,n})^2+\frac{i}{\hbar}(\vec{q}_2^{\,n}-\vec{q}_1^{\,n})\cdot\vec{P}_1^{\,n}-\frac{i\tau}{\hbar}W(\vec{r},\{q\}_2\{q\}_1,\tau)\right), \tag{33}$$

and we calculate it by using the stationary phase method. The stationary point $\vec{q}_{2,0}^{\,n}$ is determined from

$$\frac{M_S}{\hbar\tau}(\vec{q}_2^{\,n}-\vec{q}_1^{\,n})+\vec{P}_1^{\,n}-\frac{\tau}{\hbar}\frac{\partial}{\partial\vec{q}_2^{\,n}}W=0\,, \tag{34}$$

whence

$$\frac{M_S}{2\hbar\tau}(\vec{q}_{2,0}^{\,n}-\vec{q}_1^{\,n})^2=\frac{\tau}{\hbar}\frac{\hbar^2(\vec{P}_1^{\,n})^2}{2M_S}-\frac{\tau^2}{M_S}\vec{P}_1^{\,n}\cdot\left(\frac{\partial}{\partial\vec{q}_2^{\,n}}W\right)_{\vec{q}_{2,0}^{\,n}}+\frac{\tau^3}{2\hbar M_S}\left(\frac{\partial}{\partial\vec{q}_2^{\,n}}W\right)^2_{\vec{q}_{2,0}^{\,n}} \tag{35}$$

and the value of the phase at the stationary point is

$$-\frac{\tau}{\hbar}\frac{\hbar^2(\vec{P}_1^{\,n})^2}{2M_S}-\frac{\tau}{\hbar}(\overline{W}_n)_{\vec{q}_{2,0}^{\,n}}\,,$$

where

$$\overline{W}_n = W - \frac{\tau^2}{2M_S}\left(\frac{\partial W}{\partial \vec{q}_2^{\,n}}\right)^2 . \tag{36}$$

Thus, the result of the integration over $\{q\}_2$ is

$$\overline{B}(\vec{r},\{q\}_1,\tau)\exp\left[-\frac{i}{\hbar}\tau\left(\sum_{l=1}^{N}\frac{\hbar^2(\vec{P}_1^{\,l})^2}{2M_S}+\overline{W}(\vec{r},\{q\}_1,\tau)\right)\right], \tag{37}$$

where

$$\overline{W}_{l+1}=\overline{W}_l-\frac{\tau^2}{2M_S}\left(\frac{\partial \overline{W}_l}{\partial \vec{q}_2^{\,l+1}}\right)^2, \quad l=0,1,2,\ldots,N-1,$$

$$\overline{W}_0 \equiv W, \quad \overline{W}\equiv \overline{W}_N,$$

and

$$\overline{B}(\vec{r},\{q\}_1,\tau)\equiv B(\vec{r},\{q\}_{2,0}\{q\}_1,\tau)\prod_{l=0}^{N-1}\left[\frac{(-2\pi i\hbar\tau/M_S)^3}{\det[\vec{I}-\tau^2/M_S(\partial^2\overline{W}_l/\partial\vec{q}_2^{\,l+1}\vec{q}_2^{\,l+1})]}_{\vec{q}_{2,0}^{\,l+1}}\right]^{1/2}. \tag{38}$$

We now have

$$\Delta G(\vec{p}',\{q\}_b;\vec{p},\{q\}_a;\tau)\approx\sum_{m,m'}\Delta(\epsilon_{pm},\epsilon_{p'm'})\phi_{m'}(\{q\}_b)\phi_m^*(\{q\}_a)$$
$$\times\int d\vec{r}\,e^{i\vec{k}\cdot\vec{r}}\int d\tau\int d\{q\}_1\,\phi_m(\{q\}_1)\overline{B}(\vec{r},\{q\}_1,\tau)$$
$$\times\exp\left(\frac{i\tau}{\hbar}[\epsilon_p-\epsilon_{\vec{p}}+\epsilon_m-\overline{W}(\vec{r},\{q\}_1,\tau)]\right)$$
$$\times\exp\left\{-\frac{i\tau}{\hbar}\left[\sum_l\frac{\hbar^2(\vec{P}_1^{\,l})^2}{2M_S}+U(\{q\}_1)\right]\right\}\phi_{m'}^*(\{q\}_1), \tag{39}$$

and can treat $\vec{P}_1^{\,l}$ as an operator again. $H_S=\sum_l\hbar^2(\vec{P}_1^{\,l})^2/2M_S+U(\{q\}_1)$ is simply the full solid Hamiltonian. The last two factors in Eq. (39) can be written

$$e^{-(i/\hbar)H_S\tau}\phi_{m'}^*(\{q\}_1)=e^{-(i/\hbar)\tau\epsilon_{m'}}\phi_{m'}^*(\{q\}_1)$$

and the total time dependent exponential takes the form

$$\exp\left(\frac{i}{\hbar}\tau[(\epsilon_p-\epsilon_{\vec{p}}+\epsilon_m-\epsilon_{m'})-\overline{W}(\vec{r},\{q\}_1,\tau)]\right).$$

The Δ function in Eq. (38) is responsible for the conservation of the total energy during the collision, i.e.,

$$\epsilon_p+\epsilon_m=\epsilon_{p'}+\epsilon_{m'},$$

whence

$$\Delta G\approx\sum_{m,m'}\Delta(\epsilon_{pm},\epsilon_{p'm'})\phi_m^*(\{q\}_a)\phi_{m'}(\{q\}_b)$$
$$\times\int d\vec{r}\,e^{i\vec{k}\cdot\vec{r}}\int d\tau\int d\{q\}_1\phi_m(\{q\}_1)\phi_{m'}^*(\{q\}_1)\,\overline{B}(\vec{r},\{q\}_1,\tau)\exp\left(\frac{i}{\hbar}\tau[(\epsilon_{p'}-\epsilon_{\vec{p}})-\overline{W}(\vec{r},\{q\}_1,\tau)]\right). \tag{40}$$

The great benefit of the last few steps is that the time-dependent exponential in Eq. (40) becomes independent of the solid quantum numbers m, m' so that we can follow the procedure used in Sec. IV A in performing the integrations over the rest of the gas-atom variables and over time $-\tau$. Thus

$$\Delta G(\vec{p}',\{q\}_b;\vec{p},\{q\}_a,\tau)\approx\sum_{m,m'}\Delta(\epsilon_{pm},\epsilon_{p'm'})\phi_{m'}(\{q\}_b)\phi_m^*(\{q\}_a)$$
$$\times\int d\{q\}_1\int d^2\vec{R}\,\phi_m(\{q\}_1)D(\vec{R},\{q\}_1)\exp[ik_z\zeta(\vec{R},\{q\}_1)+i\vec{K}\cdot\vec{R}]\phi_{m'}^*(\{q\}_1). \tag{41a}$$

where

$$\zeta(\vec{R},\{q\}_1)=\bar{z}_0+[(\epsilon_{p'}-\epsilon_{\vec{p}})-\overline{W}(\bar{z}_0,\tau_0)]\Big/\frac{\partial}{\partial\bar{z}}\overline{W}(\bar{z}_0,\tau_0) \tag{41b}$$

$\bar{z}_0$ and τ_0 are determined from the equations

$$\hbar k_z=\tau\frac{\partial}{\partial\bar{z}}\overline{W}, \tag{41c}$$

$$\epsilon_{p'} - \epsilon_{\vec{p}} = \frac{\partial}{\partial \tau}(\tau \overline{W}) , \tag{41d}$$

and $D(\vec{\vec{R}}, \{q\}_1)$ is a smoothly varying function of $\vec{\vec{R}}$ and $\{q\}_1$ similar to $D(\vec{\vec{R}})$ of Sec. IV A.

The transition amplitude from the initial state $\vec{p}, m$ to the final one $\vec{p}', m'$ is given by

$$\Delta G(\vec{p}m, \vec{p}'m') = \Delta(\epsilon_{pm}, \epsilon_{p'm'}) \times \int d^2\vec{\vec{R}} \int d\{q\}_1 \, \phi_m(\{q\}_1) D(\vec{\vec{R}}, \{q\}_1) \times \exp[ik_z \zeta(\vec{\vec{R}}, \{q\}_1) + i\vec{K} \cdot \vec{\vec{R}}] \phi^*_{m'}(\{q\}_1) . \tag{42}$$

Squaring the transition amplitude, averaging over m and summing over m' we have for the reflection probability

$$\Phi(\vec{p}, \vec{p}') = \int d^2\vec{\vec{R}} \int d^2\vec{\vec{R}}' \, e^{i\vec{K} \cdot (\vec{\vec{R}} - \vec{\vec{R}})} \times \chi(\epsilon_p - \epsilon_{p'}, k_z, \vec{\vec{R}}\vec{\vec{R}}') \tag{43}$$

where

$$\chi(\epsilon_p - \epsilon_{p'}, k_z, \vec{\vec{R}}\vec{\vec{R}}') = \frac{1}{Z} \sum_{m, m'} e^{-\beta \epsilon_m} \delta(\epsilon_{pm} - \epsilon_{p'm'}) \times \int d\{q\} \int d\{q'\} \, D(\vec{\vec{R}}, \{q\}) D^*(\vec{\vec{R}}', \{q'\}) \phi^*_m(\{q\}) \phi^*_{m'}(\{q\}) \phi_{m'}(\{q'\}) \phi^*_m(\{q'\}) \times \exp\{ik_z[\zeta(\vec{\vec{R}}, \{q\}) - \zeta(\vec{\vec{R}}', \{q'\})]\}$$

$$= \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \, e^{-(i/\hbar)(\epsilon_p - \epsilon_{p'})t} \times \sum_{m, m'} \int d\{q\} \left[\phi^*_{m'}(\{q\}) \frac{e^{-\beta H_s}}{Tr e^{-\beta H_s}} e^{-(i/\hbar) H_s t} \phi_m(\{q\}) \; D(\vec{\vec{R}}, \{q\}) \right] \times e^{ik_z \zeta(\vec{\vec{R}}, \{q\})} \int d\{q'\} [\phi^*_m(\{q'\}) e^{(i/\hbar) H_s t} \phi_{m'}(\{q'\})] D^*(\vec{\vec{R}}', \{q'\}) \, e^{-ik_z \zeta(\vec{\vec{R}}', \{q'\})} , \tag{44}$$

where $\beta \equiv 1/k_B T$, T is the temperature and $Z = \mathrm{Tr} e^{-\beta H_s}$. Defining quantum operators by

$$\hat{D}(\vec{\vec{R}}) \phi_m(\{q\}) = D(\vec{\vec{R}}, \{q\}) \phi_m(\{q\}) , \qquad \zeta(\vec{\vec{R}}) \phi_m(\{q\}) = \zeta(\vec{\vec{R}}, \{q\}) \phi_m(\{q\}) , \tag{45}$$

we can write Eq. (44) as

$$\chi(\epsilon_p - \epsilon_{p'}, k_z, \vec{\vec{R}}\vec{\vec{R}}') = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \, e^{-(i/\hbar)(\epsilon_p - \epsilon_{p'})t} \times \sum_{m'} \langle m' | \rho(H_s) e^{-(i/\hbar) H_s t} [e^{ik_z \hat{\zeta}(\vec{\vec{R}})} \hat{D}(\vec{\vec{R}})] \, e^{(i/\hbar) H_s t} e^{-ik_z \hat{\zeta}(\vec{\vec{R}}')} | \hat{D}^\dagger(\vec{\vec{R}}') | m \rangle$$

$$= \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \, e^{-(i/\hbar)(\epsilon_p - \epsilon_{p'})t} \langle e^{ik_z \hat{\zeta}(\vec{\vec{R}}, t)} \hat{D}(\vec{\vec{R}}, t) \, e^{-ik_z \hat{\zeta}(\vec{\vec{R}}, 0)} \hat{D}^\dagger(\vec{\vec{R}}', 0) \rangle_S , \tag{46}$$

where $\langle \; \rangle_S$ denotes an ensemble average over the solid states.

The amplitude $\hat{D}(\vec{\vec{R}}, t)$ is a slowly varying function of $\{q\}$ in contrast to the exponential. We therefore neglect its $\{q\}$ dependence and, consequently, its t dependence and set it equal to an appropriate mean value $D(\vec{\vec{R}})$ so that

$$\chi(\epsilon_p - \epsilon_{p'}, k_z, \vec{\vec{R}}\vec{\vec{R}}') \approx \int_{-\infty}^{\infty} dt \, e^{-(i/\hbar)(\epsilon_p - \epsilon_{p'})t} D(\vec{\vec{R}}) D^*(\vec{\vec{R}}') \times \langle e^{ik_z \hat{\zeta}(\vec{\vec{R}}, t)} e^{-ik_z \hat{\zeta}(\vec{\vec{R}}', 0)} \rangle_S . \tag{47}$$

This correlation function is quite similar to that appearing in the theory of neutron scattering[26] or

of the Mössbauer effect.[26] There is, however, a significant difference between our problem and neutron scattering because the momentum transfer k_z in our problem is so large that it is impossible to expand the exponentials involved. This means that for a harmonic solid, multiphonon processes dominate the correlation function rather than a single phonon.[27,28] To handle such a rapidly oscillating integrand a method such as steepest descents[29] (saddle point integration) is useful.

VI. DISCUSSION AND SUMMARY

The theory presented in this article shows that the scattering process can be effectively represented in terms of a reflection from a rigid "rippling mirror."[17,30] This is true despite the smooth character of the gas-surface potential on the scale of the incident wavelength λ and despite the large amount of momentum transfer to at most a few atoms on the surface during the collision. The corresponding "rippling mirror," represented by the shape function $\zeta(\vec{R}, t)$, is, in general, not a global quantity but is determined self consistently with a specific classical trajectory with a given incident and final momenta. It becomes, however, a global quantity that is independent of initial and final momenta if the effective range of the gas-surface forces is very small compared to the amplitude of the surface corrugation. Thus, instead of applying a model for the gas-surface interaction potential in the early stages of the calculations, which in any case leads to a cumbersome procedure, we are allowed in such a situation to model the shape function $\zeta(\vec{R}, t)$. This yields a tractable procedure which could meet the challenge given by the complicated problem under consideration.

The conditions for the validity of this simple procedure are: (i) The impulse approximation should be valid. (See Sec. III). (ii) The semiclassical approximation should hold for almost every trajectory involved. In other words the stationary phase approximation for the integral over $\vec{R}$ should hold almost everywhere on the surface plane. The fulfillment of this condition requires a very large amplitude of the surface corrugation on the scale of λ. (iii) The total variation $2h$ of the surface corrugation should be much larger than c. This condition is compatible with condition (II) above. (iv) Contributions from multiple-hit trajectories should be small. A rough criterion for the occurence of multiple-hit trajectories is given in Ref. 31 for a static solid, namely $h \gtrsim 0.13a$. Thus, in contrast with conditions (II, III) this condition requires a smooth surface. To avoid any conflict between the single-hit requirement and conditions (ii) and (iii) one has to require that $c \ll 0.26a$. For Ag with $a \approx 2.88$ Å, this becomes $c \ll 0.75$ Å.

For the dynamical case under consideration the situation of multiple-hits is much more subtle than for the static case. Formally speaking, the main difficulty which arises in such a situation is the breakdown of the impulse approximation for the overall collision events. Physically, the distance traveled by the gas atom between two successive hits is of the order a, which is much longer than c. The corresponding traveling time is much longer than the period of a single hit so that the surface atoms, which are directly impinged upon by the gas atom in the first hit, could displace considerably from their initial positions, leading to a huge distortion of the surface periodicity. Furthermore, the big perturbation in momentum space created by the first hit, which remains local during the first hit, could radiate to neighboring sites during the traveling period to the second hit. Both the direct displacement and the indirect radiation effect should be very important in the second hit.

The available experimental data on the system Ar-Ag(111) indicate,[7] however, that multiple-hit contributions are not important. The reason for that is the following: multiple-hit contributions are known to enhance when the angle of incidence increases. However, the experimental width of the lobe in the angular distribution decreases with increasing angle of incidence, while enhancements in multiple-hit contributions are known to broaden the lobe's width.[32] This does not mean that the role of the surface corrugation is unimportant in the present case. A comparison of the flat hard cube model[10] with experimental data for incident energy of[7] 3.44 eV indicates the importance of the surface corrugation. This comparison shows that the hard cube prediction for the lobe's width is too narrow while the predicted location of the lobe's maximum is too much shifted from the specular direction towards the surface tangent. The wrong location of the lobe's maximum is, at least partly, due to the lack of momentum transfer parallel to the surface plane in this model while the introduction of umklapp processes parallel to the surface plane could broaden the lobe. It is thus impossible to ignore corrugation.

Finally, we should note that arguments like those appearing above might be meaningless without considering the possibility of electronic excitations on the surface.

ACKNOWLEDGMENTS

This work has been supported by NSF Grant No. DMR77-07723. We also acknowledge helpful discussions with Professor L. Wharton, Professor R. Gomer, and Professor V. Celli.

*Present address: Dept. of Chemistry, Univ. of California, Santa Barbara, Calif. 93106.

[1]I. Esterman and O. Stern, Z. Phys. 61, 95 (1930).
[2]J. D. McClure, J. Chem. Phys. 52, 2712 (1970).
[3]J. E. Lennard-Jones and A. F. Devonshire, Nature (London) 137, 1069 (1936).
[4]F. O. Goodman and H. Y. Wachman, "Dynamics of Gas-Surface Scattering" (Academic, New York, 1976), p. 232.
[5]M. W. Cole and D. R. Frankl, Surf. Sci. 70, 585 (1978).
[6]L. Wharton (private communication).
[7]M. J. Romney and J. B. Anderson, J. Chem. Phys. 51, 2490 (1969).
[8]W. J. Hays, Ph.D. thesis (Univ. of California, Los Angeles, 1970) (unpublished).
[9]D. R. Miller and R. B. Subbarao, J. Chem. Phys. 52, 425 (1970); R. B. Subbarao and D. R. Miller, *ibid.* 58, 5247 (1973).
[10]R. M. Logan and R. E. Stickney, J. Chem. Phys. 44, 195 (1966).
[11]R. A. Oman, J. Chem. Phys. 48, 3919 (1968).
[12]J. D. Doll, J. Chem. Phys. 61, 954 (1974); Chem. Phys. 3, 257 (1974).
[13]R. I. Masel, R. P. Merrill, and W. H. Miller, J. Chem. Phys. 64, 45 (1976).
[14]U. Garibaldi, A. C. Levi, R. Spadacini, and G. E. Tommei, Surf. Sci. 48, 649 (1975).
[15]R. I. Masel, R. P. Merrill, and W. H. Miller, Phys. Rev. B 12, 5545 (1975).
[16]N. R. Hill and V. Celli (unpublished).
[17]M. V. Berry, J. Phys. A 8, 566 (1975).
[18]R. P. Feynmann and A. R. Hibbs, "Quantum Mechanics and Path Integrals" (McGraw-Hill, New York, 1965).
[19]P. A. Dirac, "The Principles of Quantum Mechanics" (Clarendon, Oxford, 1947).
[20]W. H. Miller, Adv. Chem. Phys. 25, 69 (1974).
[21]R. Balian and C. Bloch, Ann. Phys. 63, 592 (1971).
[22]The absence of a first-order term in τ as well as of higher odd powers is due to time-reversal symmetry.
[23]This term does not contribute to the reflection probability within the stationary phase approximation.
[24]P. Choquard, Helv. Phys. Acta 28, 89 (1955).
[25]M. V. Berry and K. E. Mount, Rep. Prog. Phys. 35, 315 (1972).
[26]C. Kittel, "Quantum Theory of Solids" (Wiley, New York, 1963).
[27]N. Cabrera, V. Celli, and R. Manson, Phys. Rev. Lett. 22, 346 (1969).
[28]J. L. Beeby, J. Phys. C 5, 3438 (1972).
[29]P. M. Morse and H. Feshbach "Methods of Theoretical Physics" (McGraw-Hill, New York, 1953), p. 434.
[30]U. Garibaldi, A. C. Levi, R. Spadacini, and G. E. Tommei, Surf. Sci. 38, 269 (1973).
[31]R. I. Masel, R. P. Merrill, and W. H. Miller, J. Chem. Phys. 65, 2690 (1976).
[32]A word of caution should be added here since at large incident angles shadowing of the valleys in the corrugation makes the surface effectively flatter and may reduce the width of the lobe.